

Dimethylthallium(III) Derivatives of Decaborane(14)

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Summary Reaction of trimethylthallium with decaborane (14) yields the simple salt $[\text{Me}_2\text{Tl}]^+[\text{B}_{10}\text{H}_{13}]^-$, (A), and the complex $[\text{Me}_2\text{Tl}]^+[\text{B}_{10}\text{H}_{12}\text{TlMe}_2]^-$, (B), which contains two distinct dimethylthallium(III) groups, one of which is chelated by the dodecahydro-*nido*-decaborate ($2-$) ion.

THERE is considerable current interest in Group III_B derivatives of boron hydrides and carboranes; however, although several have recently been characterised,¹⁻⁴ no thallium derivatives of either boron hydrides or carboranes have been reported. We here present results on the formation and properties of organo-thallium(III) derivatives of decaborane (14), one of which in particular shows unusual structural features.

Deprotonation of decaborane by trimethylthallium in diethyl ether at room temperature yields the two dimethylthallium derivatives $[\text{Me}_2\text{Tl}]^+[\text{B}_{10}\text{H}_{13}]^-$, (A),† and $[\text{Me}_2\text{Tl}]^+[\text{B}_{10}\text{H}_{12}\text{TlMe}_2]^-$, (B).† Both (A) and (B) react with an excess of hydrogen chloride in diethyl ether to generate stoichiometric amounts of Me_2TlCl and $\text{B}_{10}\text{H}_{14}$.

Compound (A) is formulated as such on the basis of its proton n.m.r. spectrum (which shows only the presence of ionic Me_2Tl^+)⁵ and its ¹¹B n.m.r. spectrum (which is identical to that of $\text{B}_{10}\text{H}_{13}^-$).⁶ Compound (B) exists in non-aqueous polar solvents as $[\text{Me}_2\text{Tl}]^+[\text{B}_{10}\text{H}_{12}\text{TlMe}_2]^-$, as shown by molecular-weight and conductivity studies, and by the proton n.m.r. spectrum (Figure 1) which shows the presence of *one* Me_2Tl^+ ion and *one* covalently bound Me_2Tl group.

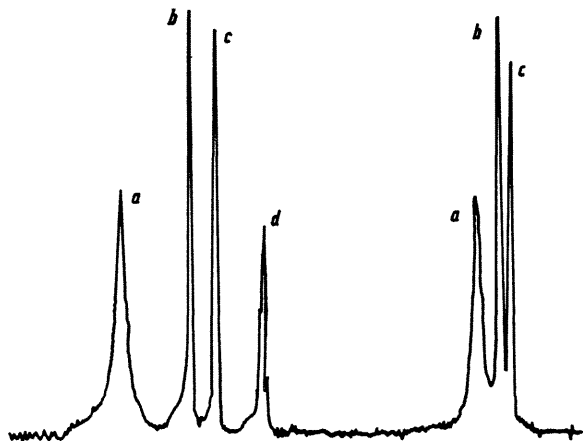


FIGURE 1. The 60 MHz proton n.m.r. spectrum of $[\text{Me}_2\text{Tl}]^+[\text{B}_{10}\text{H}_{12}\text{TlMe}_2]^-$ in dry $[\text{C}_6\text{H}_6][\text{Me}_2\text{CO}]$ at 33°, (assignment of coupling constants is verified by spectra obtained at both 90 and 220 MHz) τ (relative to tetramethylsilane)/p.p.m. (J/Hz): (a) 8.58 (402); (b) 9.44 (348); (c) 9.78 (332); (d) solvent.

† Satisfactory analytical data have been obtained for these compounds.

¹ N. N. Greenwood and J. A. McGinnety, *Chem. Comm.*, 1965, 331; *J. Chem. Soc. (A)*, 1966, 1090.

² B. M. Mikhailov and T. V. Potapova, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1968, 5, 1153; M. R. Churchill, A. H. Reis, D. A. T. Young, G. R. Willey, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1970, 92, 6663; *Chem. Comm.*, 1971, 298.

³ R. N. Grimes and W. J. Rademaker, *J. Amer. Chem. Soc.*, 1969, 91, 6498.

⁴ R. N. Grimes, *J. Amer. Chem. Soc.*, 1971, 93, 261.

⁵ G. D. Shier and R. S. Drago, *J. Organometallic Chem.*, 1966, 5, 330.

⁶ J. Q. Chambers, A. D. Norman, M. R. Bickell, and S. H. Cadle, *J. Amer. Chem. Soc.*, 1968, 90, 6056.

⁷ N. N. Greenwood, J. A. McGinnety, and J. D. Owen, *J. Chem. Soc. (A)*, 1971, 809.

The doublet corresponding to Me_2Tl^+ is somewhat broadened but is equal in intensity to the sum of the other two doublets. The existence of *two* doublets of equal intensity for the covalent Me_2Tl function suggests that the two methyl groups are in different environments, and that $\text{B}_{10}\text{H}_{12}\text{TlMe}_2^-$ may have a structure such as that in Figure 2, where the

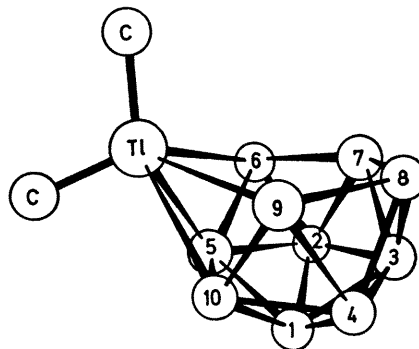


FIGURE 2. Proposed heavy-atom structure of the $\text{B}_{10}\text{H}_{12}\text{TlMe}_2^-$ ion; numbering as in decaborane(14). Each boron atom carries one external hydrogen atom and there are bridging hydrogen atoms between B_6-B_7 and between B_8-B_9 .

dodecahydro-*nido*-decaborate ($2-$) ion, $\text{B}_{10}\text{H}_{12}^{2-}$ acts as a formal bidentate ligand towards Me_2Tl^+ . [A recent single crystal X-ray study has shown that the $\text{B}_{10}\text{H}_{12}^{2-}$ ligand behaves in an analogous manner toward Zn^{2+} in the complex ion $\text{Zn}(\text{B}_{10}\text{H}_{12})_2^{2-}$.⁷ Similarly, the ¹H n.m.r. spectrum of the salt, $[\text{Ph}_3\text{PMe}]^+[\text{B}_{10}\text{H}_{12}\text{TlMe}_2]^-$, (C)† {isolated from the stoichiometric reaction of $[\text{Ph}_3\text{PMe}]^+\text{Br}^-$ with (B) in dichloromethane-tetrahydrofuran} indicates the presence of only a covalently bound Me_2Tl group and, as in (B), the two doublets are assigned to two non-equivalent methyl groups bound to thallium. In contrast to its behaviour in non-aqueous polar solvents, (B) dissolves in water to form Me_2Tl^+ (as shown by ¹H n.m.r.) and $\text{B}_{10}\text{H}_{12}^{2-}$ ions; from such aqueous solutions, Me_2TlBr , and $[\text{Ph}_3\text{PMe}]_2^+[\text{B}_{10}\text{H}_{12}]^{2-}$ † can be obtained in almost quantitative yield by reaction firstly with sodium bromide and then with $[\text{Ph}_3\text{PMe}]^+\text{Br}^-$.

The n.m.r. spectra of metal-boron hydride derivatives often give little insight into their structure; however, it appears that in compounds containing the Me_2Tl group, the use of proton n.m.r. spectroscopy may yield more structural information than is normally obtainable. We are at present investigating the use of the Me_2Tl group as a structural indicator in its derivatives with other boron hydrides.

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